RELATIONSHIP BETWEEN THE GASIFICATION REACTIVITIES OF COAL CHAR AND THE PHYSICAL AND CHEMICAL PROPERTIES OF COAL AND COAL CHAR

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INTRODUCTION

A variety of experimental investigations have studied, at elevated pressures, the gasification kinetics of coal chars in hydrogen and in gases containing steam and hydrogen. The bulk of these investigations, however, have been primarily concerned with the characterization of gasification rates as a function of environmental conditions such as temperature, pressure, and gas composition, and have provided little systematic information concerning relationships between gasification reactivities and the physical and chemical properties of coal or coal char.

This study was therefore initiated to evaluate possible relationships between gasification reactivities and simple compositional parameters for coal chars derived from a wide variety of coals and coal-maceral concentrates. The internal structural changes that occur during the course of gasification of a few coal chars of varying rank were also explored. The gasification reactivities of individual coal chars were determined in hydrogen or in a 50:50 steam-hydrogen mixture at 35 atmospheres, using a high-pressure thermobalance. Most tests were conducted at 1700°F, although, in a special series of tests designed to investigate the catalytic effects of exchangeable cations on lignite char reactivities, temperatures were varied from 1400° to 1700°F. The following results are discussed in this paper:

- The relationship between the initial carbon content and the gasification reactivities determined in the hydrogen at 1700°F, for coal chars derived from 36 coals and maceral concentrates ranging in rank from anthracite to lignite.

- The effect of exchangeable cation concentrations (sodium and calcium) on gasification reactivities of lignites in hydrogen at 1700°F and in steam-hydrogen mixtures at 1400° to 1700°F.

- The surface area and pore volume variations that occur during gasification in hydrogen and in steam-hydrogen mixtures at 1700°F of coal chars derived from anthracite, metallurgical coking coal, high-volatile A bituminous coal, sub-bituminous A coal, and lignite.

EXPERIMENTAL PROCEDURE

The high-pressure thermobalance used in this work to obtain gasification reactivity factors has been described previously (4). The main feature of this apparatus is that the weight of a small fixed-bed sample of coal char (1/2 to 1 gram) contained in a wire-mesh basket can be continously measured as it undergoes gasification in a desired gaseous environment at constant temperature and pressure. In all tests conducted, −20+40 U.S. sieve size particles were used, and gas flow rates in the reactor were maintained at sufficiently high values to result in negligible gas conversion. Under these conditions, coal-char gasification could be considered to occur under constant known environmental conditions. Coal chars were produced by initially exposing the raw coals to nitrogen at 1 atmosphere for

60 minutes, at the same temperature to be used during subsequent gasification in hydrogen or in steam-hydrogen mixtures. The weight loss versus time characteristics obtained during gasification in individual tests were then used as a basis for computing gasification reactivity factors, using a procedure described below.
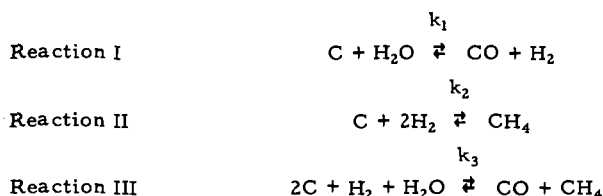
Certain of the solid feeds and residues were analyzed for internal surface area, pore volume, and true density. Surface areas were computed from adsorption isotherms obtained with a Model 2100 Orr surface area-pore volume analyzer manufactured by the Micromeretics Corp., which was also used to obtain true densities in helium. Adsorption isotherms obtained in nitrogen at 77°K were interpreted with the BET equation to compute surface area, and isotherms obtained in carbon dioxide at 298°K were interpreted with the Dubinin-Polanyi equation as modified by Kaganer (7) to compute surface area. In general, surface areas computed from nitrogen and carbon dioxide adsorption isotherms were not in agreement, and values obtained in carbon dioxide were considered to be most reflective of equivalent internal surface area, which is consistent with the findings of other investigators (2, 3, 6, 7, 12). Apparently, the penetration of nitrogen into the microporous structure of coals or carbonized coal chars is severely limited by slow, activated diffusion processes at 77°K, leading to very low apparent surface areas; on the other hand, for partially gasified coal chars having more open microporous structures, capillary condensation of nitrogen can lead to unreasonably high apparent surface areas (1, 8). Adsorption isotherms obtained with carbon dioxide at the higher temperature of 298°K facilitate activated diffusion into microporous structures, and capillary condensation is inhibited by the lower relative pressures employed (0.003 to 0.02). Although there is some question concerning whether carbon dioxide adsorption isotherms should be interpreted in terms of micropore volume (8, 9, 10, 11) rather than micropore surface area (2, 3, 6, 7, 12), the distinction is not of importance in empirical correlations with gasification kinetic parameters. This is because the calculation methods used to compute numerical values of micropore volume and micropore surface area are virtually identical, differing only in the numerical constants used. Thus, reported values of micropore volumes can be converted to corresponding values of micropore surface area by a fixed constant. In this study we have chosen to compute surface area values, favoring the argument that carbon dioxide adsorption on a carbon surface should be restricted to a monolayer thickness, as a result of the quadruple interaction of the carbon dioxide molecules with the π-bonds of the carbon surface (2, 7).

An Aminco mercury intrusion porosimeter capable of a hydrostatic pressure of 15,000 psi was used to obtain pore volume distributions for pores having diameters greater than about 120 angstroms. Pore volume distributions for pores between about 12 and 300 angstroms were obtained from adsorption isotherms obtained in nitrogen at 77°K at relative pressures up to about 0.93. Good agreement was obtained with these two methods in the overlap region from 180 to 300 angstroms, similar to results reported by Gan et al. (3).

DEFINITION OF RELATIVE REACTIVITY FACTOR, f_L

Weight loss versus time characteristics obtained in individual thermobalance tests were interpreted to obtain relative reactivity factors for the coal chars used, based on a quantitative model developed previously at the Institute of Gas Technology to describe the gasification kinetics of bituminous coal chars as a function of temperature, pressure, gas composition, pretreatment temperature, and carbon conversion (4). The essential features of this model are described below.

Coal-char gasification in gases containing steam and hydrogen are assumed to occur via three main reactions:

		k_1	
Reaction I		$C + H_2O \rightleftarrows CO + H_2$	

		k_2	
Reaction II		$C + 2H_2 \rightleftarrows CH_4$	

		k_3	
Reaction III		$2C + H_2 + H_2O \rightleftarrows CO + CH_4$	

where k_1, k_2, and k_3 are rate constants for the three reactions shown and are quantitatively defined in the model as a function of temperature, pressure, and gas composition (accounting for CO, H_2, H_2O, and CH_4). The differential coal-char conversion rate is expressed by the relationship:

$$\frac{dX}{d\theta} = f_L k_T (1 - X)^{2/3} \exp (-\alpha X^2) \qquad 1)$$

where —

X = base carbon conversion fraction

θ = time

f_L = relative reactivity factor for coal-char gasification, which depends on the particular coal char and on the pretreatment temperature used in preparing the coal char

k_T = $k_1 + k_2 + k_3$

α = kinetic parameter defined as a function of pressure and gas composition.

"Base carbon," referred to in the above definition of X, means the nonvolatile carbon in raw coal that remains after standard devolatilization. Base carbon conversion fractions can be estimated from weight loss-versus-time curves obtained in thermobalance tests, using the expression:

$$X = \frac{(W/W_0 - VM)}{1 - VM - A} \qquad 2)$$

where —

W/W_0 = total weight-loss fraction referred to original coal

VM = weight loss fraction during initial devolatilization in nitrogen (approximately equal to standard volatile matter at elevated temperature)

A = ash mass fraction in feed coal.

The relative reactivity factor, f_L, depends on the pretreatment temperature according to the expression:

$$f_L = f_o \exp (8467)(1/T_p - 1/T) \qquad 3)$$

where —

f_o = reactivity factor dependent only on the inherent nature of the coal char

T_p = pretreatment temperature, °R

T = gasification temperature, °R.

Equation 3 is only applicable for $T_p > T$; for $T_p \leq T$, then $f_L = f_o$.

At constant environmental conditions, Equation 1 can be integrated to yield —

$$M(X) = \int_o^X \frac{\exp(\alpha X^2)}{(1-X)^{2/3}} \, dX = f_L k_T \theta \qquad 4)$$

Based on Equation 4, a plot of $M(X)$ versus θ should yield a straight line having a slope equal to the term $f_L k_T$. Values of $M(X)$ can be computed from experimental thermobalance data, using Equation 2 to obtain values of X and using the defined value of α to evaluate the integral in Equation 4. Note that, for tests conducted in pure hydrogen, the value of α is 0.97; with this value, the term $(1-X)^{2/3}\exp(0.97\,X^2)$ is approximately equal to $(1-X)$, over nearly a complete range of X. For this case, $M(X) = -\ln(1-X)$ and values of the specific gasification rate, $(dX/d\theta)/(1-X)$, are constant and equal to $f_L k_T$.

Figure 1 shows two types of behavior noted in this study in experimental plots of $M(X)$ versus θ. Line A is typical of the characteristics obtained with the majority of coal chars tested, with linearity exhibited over the complete range of base carbon conversion. The line shown does not extrapolate to the origin because char samples initially exposed to the gasifying environment in the thermobalance require 1 to 2 minutes to heat up to reactor temperature. A characteristic of the type shown for Case B was obtained with some coal chars, usually low-rank materials, indicating an initial period of transient reactivity, which decreased during the first 5 to 10 minutes and remained constant thereafter. For coal chars exhibiting this type of behavior, only the linear portion of the curve corresponding to constant reactivity was used to evaluate experimental values of $f_L k_T$.

Values of the reactivity factor, f_L, were then obtained by dividing the term $f_L k_T$ by the value of k_T defined in the model (4) for the reaction conditions used.

RESULTS

Correlation of Reactivity Factors With Carbon Content in Raw Coals

The reactivity factors for coal chars derived from 36 coals and coal maceral concentrates were determined in hydrogen at 1700°F and 35 atmospheres. The distribution of coals used with respect to rank and lithotype is described in Table 1. In this study a variety of correlations were evaluated in attempting to quantitatively relate these reactivity factors with simple, compositional parameters included in ultimate, proximate, and petrographic analyses of the raw coals. The best success, however, was achieved with one of the simplest correlations considered — a relationship between reactivity factors and initial carbon contents. This correlation is illustrated in Figure 2, where the line drawn corresponds to the expression:

$$f_L = 6.2Y(1-Y) \qquad 5)$$

where —

f_L = relative reactivity factor of coal char

Y = concentration of carbon in raw coal (dry, ash-free), g/g coal.

Table 1. NUMBERS OF EACH COAL TYPE USED IN CORRELATION

Coal Rank	Whole	Vitrain	Fusian	Total
Lignite	1	1	1	3
Subbituminous C	2	1	--	3
Subbituminous B	1	2	2	5
Subbituminous A	3	2	1	6
High-Volatile C Bituminous	1	2	1	4
High-Volatile B Bituminous	1	1	4	6
High-Volatile A Bituminous	4	2	--	6
Low-Volatile Bituminous	2	--	--	2
Anthracite	1	--	--	1
Total	16	11	9	36

For reasons discussed below, it should be emphasized that, for lignite coal chars, the correlation shown in Figure 2 is applicable only when the raw lignite is initially treated in acid to remove exchangeable cations.

The standard deviation of experimental reactivity factors shown in Figure 2 and of reactivity factors calculated from Equation 5 is about 0.1, which is equivalent to the reproducibility of experimentally determined reactivity factors. Interestingly, the correlation proposed does not uniquely distinguish between maceral types.

Effects of Exchangeable Cation Concentration on Lignite Char Reactivity

If reactivity factors determined for coal chars derived from untreated raw lignites were included in Figure 2, then a considerable amount of scatter would be apparent above the correlation line at low carbon concentrations. One phase of this study, however, showed that the reactivities of lignite chars obtained from lignites initially treated in HCl or HCl-HF acid were generally significantly less than the corresponding reactivities exhibited by lignite chars derived from untreated lignites. This was not observed with several bituminous and subbituminous coal chars. This behavior apparently resulted from a catalytic effect of exchangeable cations inherently present in raw lignites in carboxyl functional groups, which can be removed in acid by the following type of reaction:

$$-COONa + H^+ = -COOH + Na^+$$
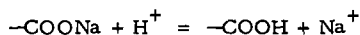
With this explanation, one can reasonably expect that this catalytic effect would predominate in lignites and would decrease rapidly with increasing coal rank, corresponding to a rapid decrease in the amount of coal oxygen combined in carboxyl functional groups.

A series of tests were conducted to obtain a quantitative measure of the effects of exchangeable cation concentration (sodium and calcium) on char reactivity factors for gasification in hydrogen and in steam-hydrogen mixtures. These tests were conducted with lignite chars derived from raw lignites, with the lignite chars derived from raw lignites initially demineralized in hydrochloric acid to remove exchangeable cations and with the lignite chars derived from raw lignites initially demineralized in hydrochloric acid to which various amounts of calcium or sodium were then added by cation exchange in sodium acetate or calcium acetate solutions. Results of one

series of tests corresponding to gasification in hydrogen at 1700°F are shown in Figure 3. The results in Figure 3 were correlated with the expression:

$$f_L/f_L^o = 1 + 54.7 \, Y_{Na} + 14.0 \, Y_{Ca} \qquad\qquad 6)$$

where —

f_L = reactivity factor of lignite to which sodium or calcium was added

f_L^o = reactivity factor of acid-treated lignite (Y_{Na}, Y_{Ca} = 0)

Y_{Na}, Y_{Ca} = concentration of exchangeable sodium or calcium in lignite before devolatilization in nitrogen, g/g fixed carbon.

Although the correlation given in Equation 6 was developed from data obtained with prepared lignites that did not contain both calcium and sodium at the same time, it does apply reasonably well to untreated lignites containing, in some cases, both calcium and sodium. This is demonstrated in Table 2.

Table 2. COMPARISON OF CALCULATED AND
EXPERIMENTAL REACTIVITY RATIOS

Lignite	Y_{Ca}	Y_{Na}	f_L/f_L^o	
	g/g fixed carbon		Calculated	Experimental
Savage Mine, Montana (whole)	0.043	0.000	2.1	1.7
Savage Mine, Montana (vitrain)	0.019	0.004	1.5	1.7
Glenharold Mine, N. Dakota (whole)	0.031	0.009	1.9	2.0
Glenharold Mine, N. Dakota (vitrain)	0.019	0.002	1.3	1.2

A test series was also conducted to determine effects of exchangeable calcium and sodium concentrations on the reactivities on a Montana lignite char in steam-hydrogen mixtures at temperatures from 1400°F to 1700°F. Results obtained are illustrated in Figure 4, which plots values of the kinetic term, $f_L k_T$, as a function of temperature and cation concentration. Although these results have not yet been quantitatively correlated, they apparently show that sodium and calcium significantly enhance gasification in steam-hydrogen mixtures, even more so than for gasification in hydrogen alone. Figure 4 shows that the effect of calcium concentration on reactivities is substantially the same as the effect of sodium concentration at corresponding conditions (contrary to the behavior obtained in pure hydrogen), and that relative catalytic effects tend to decrease with increasing gasification temperature.

A significant additional result of the test series conducted with steam-hydrogen mixtures was that the reactivity of acid-treated Montana lignite (Y_{Ca}, Y_{Na} = 0) remains constant for gasification in steam-hydrogen mixtures over a temperature range from 1400° to 1700°F. This is shown in Figure 5, which plots experimental values of $f_L k_T$ versus values of k_T calculated from correlations developed to describe bituminous coal char gasification kinetics (4). The line drawn corresponds to a constant value of f_L = 1.3, which is about the same value obtained for gasification in pure hydrogen at 1700°F.

Variations in Internal Char Surface Areas During Gasification

The variations in internal surface areas were measured for several chars at different stages of gasification in hydrogen or steam-hydrogen mixtures. The compositions of the coals from which these chars were prepared are given in Table 3. Figure 6 shows the variations in surface area measured in carbon dioxide with different base carbon conversion fractions for a series of tests conducted with Montana lignite chars. Figure 6 shows that the internal surface area of the Montana lignite char tends to remain constant over a major range of base carbon conversion fractions and is essentially independent of char pretreatment or gasification conditions. The apparent surface areas of carbonized chars $(X = 0)$ are lower than the nominal value of partially gasified chars. This difference may reflect that, even with carbon dioxide, penetration into the micropore structure is somewhat inhibited before the structure is opened up by partial gasification.

Figure 7 shows variations in apparent surface area measured in nitrogen for Montana lignite chars. The characteristics shown tend to support the suggestion made previously that, at low levels of conversion, nitrogen penetration into the micropore structure is severly inhibited, but that, at higher carbon conversions, unreasonably high apparent surface areas are obtained because of capillary condensation.

In Figure 8, variations in surface area measured in carbon dioxide (S_{CO_2}) obtained with some other coal chars are compared with results obtained with Montana lignite chars. Although surface areas measured for char derived from anthracite, high-volatile bituminous coal, and lignite remained essentially constant during the course of conversion in hydrogen and steam-hydrogen mixtures, surface areas for the subbituminous coal char generally decreased with increasing carbon conversions during gasification in hydrogen. Interestingly, of the four coal chars tested, only the subbituminous coal char exhibited decreasing specific gasification rates during gasification with hydrogen that paralleled the decrease in surface area. This is shown in Figure 9. Although generalizations based on the kinetic behaviors exhibited by only four coal chars are not justified, these results do suggest that a form of kinetic correlation to describe coal-char gasification rates that is more meaningful than that derived from the Equation 1 may be the following:

$$\frac{dX}{d\theta} = \lambda \; Sk_T(1 - X) \qquad\qquad 7)$$

where —

λ = relative reactivity per unit of internal surface area

S = internal surface area per mass of carbon present.

With this interpretation, the constancy of the values of f_L and S_{CO_2} of anthracite, high-volatile bituminous, and lignite coal char during gasification in hydrogen corresponds to a constant value of λ for each char. For the subbituminous coal char, λ is also constant, although S_{CO_2} decreases with increasing carbon conversion, apparently because of the growth of crystallites. For the gasification temperatures used, this growth is probably unusual and not characteristic of most coal chars. This is particularly true if the first-order kinetics observed in a variety of previous studies of the gasification of a fairly large number of coal chars in hydrogen are assumed to correspond to constant values of λ and S_{CO_2} for the individual coal char tested.

Table 3. COMPOSITIONS OF COALS USED IN PHYSICAL PROPERTY STUDIES

	Anthracite	Pittsburgh No. 8 (Ireland Mine) (Air-Pretreated)	Brazilian Carvao Metallurgical	Rosebud, Colstrip Mine	Savage Mine (Montana)
Coal Identification					
Rank	Anthracite	hvAb		Subbituminous A	Lignite
Lithotype	Whole	Whole	Whole	Vitrain	Whole
Ultimate Analysis, mass %					
Carbon	83.40	69.47	66.70	69.60	65.13
Hydrogen	2.37	3.78	4.57	4.52	4.13
Oxygen	2.62	6.59	4.57	19.31	24.20
Nitrogen	0.84	1.39	1.22	0.99	0.89
Sulfur	1.03	3.75	1.90	0.65	0.57
Ash	9.74	15.02	21.04	4.93	5.08
Total	100.00	100.00	100.00	100.00	100.00
Proximate Analysis, mass % (dry)					
Volatile Matter	6.77	22.70	31.80	42.10	43.62
Fixed Carbon	83.49	62.28	47.20	53.00	51.30
Ash	9.74	15.02	21.00	4.90	5.08
Total	100.00	100.00	100.00	100.00	100.00

Interestingly, in the kinetic model previously referred to, the value of α in Equation 1 is approximately 1.7 for a variety of gas compositions containing steam and hydrogen at elevated pressures. Empirically, this value corresponds to decreasing values of λ with increasing carbon conversions when interpreted in terms of Equation 7. This occurs even when the total internal surface areas remain constant during conversion in steam-hydrogen mixtures, as was shown in Figure 6 for Montana lignite char.

Some additional evidence was obtained in this study that can be interpreted in terms of the formulation given in Equation 7. Figure 10 shows values of S_{CO_2} obtained during gasification of a coal char derived from Brazilian metallurgical coal, at various temperatures, with hydrogen and steam-hydrogen mixtures. With this material, the char surface area, S_{CO_2}, is not a function of carbon conversion level and is the same in hydrogen and in steam-hydrogen mixtures, but decreases with increasing gasification temperature. The reactivity factor, f_L, which is characteristic of results obtained at a specific temperature, also decreases with increasing temperature and is proportional to internal char surface area, as shown in Figure 11. This particular char can then be considered to have a constant value of λ, independent of temperature, conversion, or gasification medium, but does exhibit a decreasing internal surface area with increasing temperature, a feature that probably reflects its use as a metallurgical coking coal.

Variations in Char Pore Volumes During Gasification

Figure 12 illustrates typical pore-volume distributions of partially gasified coal chars. With the exception of untreated Montana lignite (Curve F), the features exhibited in Figure 12 appear to be generally similar to the distributions obtained by Stacy and Walker (9) with some coal chars resulting from a fluid-bed hydrogasification. Whereas Curves A through E tend to show a plateau at a pore diameter of about 55 angstroms, possibly indicative of the lack of development of significant transitional pores, Curve F shows a significant variation in pore volume through this range of pore diameters. It may be pertinent, therefore, that the gasification rates of untreated Montana lignite char in a steam-hydrogen mixture were about 7 times faster than the largest of the gasification rates obtained with chars corresponding to Curves A through E. It is thus possible that, with sufficiently large gasification rates, dynamic modifications that tend to occur within coal structures as carbon is removed are inhibited.

The plateau in pore-volume variations at a pore diameter of 55 angstroms exhibited by most coals tested has suggested the following simplified representation of pore-volume characteristics: Total pore volume accessible via pores less than 55 angstroms is defined as "micropore" volume, and pore volume accessible via pore openings having diameters between 55 and 20,000 angstroms is defined as "macropore" volume. Micropore and macropore volumes obtained with different coal chars are shown in Figures 13 and 14 as a function of the base carbon conversion fraction. Note that in these figures, volumes are represented per mass of initial base carbon rather than per mass of remaining carbon and, therefore, are proportional to volumes on a per particle basis. Figure 13 shows surprisingly little variation in macropore volume with increasing conversion for Curves A through E. In viewing these results, remember that the true density of base carbon in these coal chars is about 2 grams/cu cm, corresponding to a total volume of 0.5 cu cm/gram of initial base carbon. Thus, if the space initially occupied by gasified base carbon were added to the macropore volume, macropore volumes would increase significantly with increasing carbon conversion. The results shown in Figure 13, however, indicate that this is not generally the case, with the exception of Curve F, which does show a sharp increase in macropore volume up to conversions of about 0.8.

Figure 14 shows that micropore volumes tend to initially increase with increasing carbon conversion, reach a maximum, and then decrease with increasing conversion, approaching zero at complete conversion. Interestingly, the micropore-volume characteristics corresponding to untreated Montana lignite char gasified in a steam-hydrogen mixture are essentially identical to the characteristics for the other Montana lignite chars, as opposed to the behavior noted in Figures 12 and 13. Thus, the rapid gasification rates that evidently affect structural transitions at a "macro" level apparently do not affect structural transitions on a "micro" level. This is consistent with the results discussed previously, which showed an insensitivity in lignite-char-surface areas to initial acid treatment or to gasification conditions.

The variations in total particle volume with base carbon conversion measured with the mercury porosimeter are shown in Figure 15. The volumes represent the sum of solid volume plus pore volumes accessible via pore openings having diameters of less than 120 microns. As indicated in Figure 15, total particle volumes tend to decrease with increasing base carbon conversion fraction, particularly at conversions greater than about 0.5. Because these results were somewhat unexpected when initially observed, some additional tests were conducted to obtain photographic evidence of quantitative changes that occurred in individual external coal-char particle dimensions before and after gasification in hydrogen at 1700°F. In this series of tests, a few particles each of anthracite, high-volatile A bituminous coal, and Montana lignite were initially photographed in several orientations under optically calibrated conditions; were gasified in the thermobalance to relatively high levels of carbon conversion; and were then photographed again. Detailed examination of the photographs obtained did show a significant reduction in particle volumes, consistent with the results shown in Figure 15. The fraction of volume reduction of each type of char was independent of initial particle diameter in the range from about 200 to 800 microns. This fact and the fact that external topological characteristics remained unchanged except for a diminishment in size indicated that the observed shrinkage occurred throughout individual particles and was not the result of a "shrinking core" phenomenon.

SUMMARY AND CONCLUSIONS

The overall evidence obtained in this study suggests the tentative conclusion that gasification of coal chars with hydrogen and steam-hydrogen mixtures occurs primarily at char surfaces located within micropores. This conclusion is supported by the relationships indicated between specific gasification rates and internal char surface areas, particularly for gasification in hydrogen. With the majority of coal chars, internal surface area remains constant during gasification and is independent of gasification conditions, possibly indicating an invariance in average crystallite dimensions during the gasification process. With some coal chars, however, surface areas tend to decrease with increasing conversion or increasing gasification temperature, which would be indicative of a growth in crystallite dimensions.

Particle shrinkage occurs during coal-char gasification,due almost solely to contraction of the microporous phase (solids plus pores accessible via openings with diameters less than 55 angstroms), possibly because of the continuous reorientation of individual carbon crystallites. Macropore cavities also shrink at higher levels of conversion, but in a manner analogous to cavities in a metallic solid undergoing thermal contraction. Although accessible macropore volumes may increase somewhat during the initial stages of conversion, this increase may correspond to an increasing accessibility of the macropore cavities present initially. Although there are some significant differences in the variations in surface areas and pore volumes for various coal chars during gasification, the different coal chars tested exhibit a surprising similarity in variations in average micropore diameter with increasing base carbon conversion. This is shown in Figure 16, which plots

values of the average micropore diameter, $\overline{D}$, versus the base carbon conversion fraction, X. The average micropore diameter was computed from the expression —

$$\overline{D} = \frac{4V}{S_{CO_2}}$$

where —

V = micropore volume (accessible pore-opening diameter <55A).

Although the relative gasification reactivity factor, f_L, can be considered to be the product of two terms — "char surface area" and "reactivity per unit of char surface area" — this study has not produced enough data to evaluate correlations between these separate parameters and other coal properties.

The study has shown, however, that f_L itself correlates well with the initial carbon content of raw coals for most of the coal chars tested. Lignites represent a special case, because of the catalytic effects of exchangeable cations, particularly sodium and calcium, which predominate in lignites because carboxyl functional groups are present. This catalytic effect is greater for gasification in steam-hydrogen mixtures than in hydrogen alone and tends to decrease with increasing gasification temperature.

ACKNOWLEDGMENT

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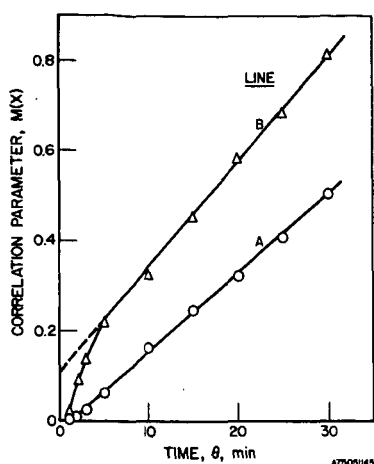12. Walker, P. L. and Patel, R. L., Fuel 49 (1), 91 (1970).

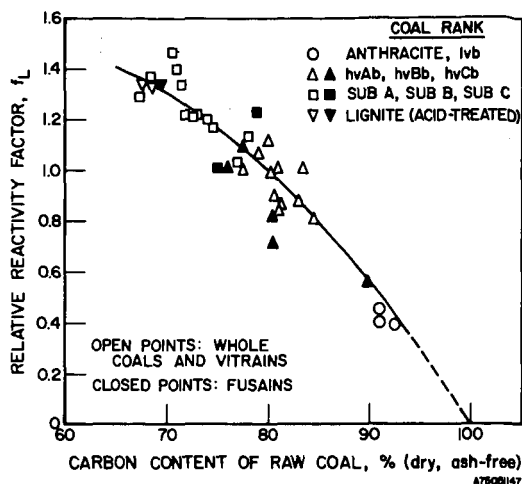Figure 1.   TYPES OF COR-
RELATION CHARACTERISTICS
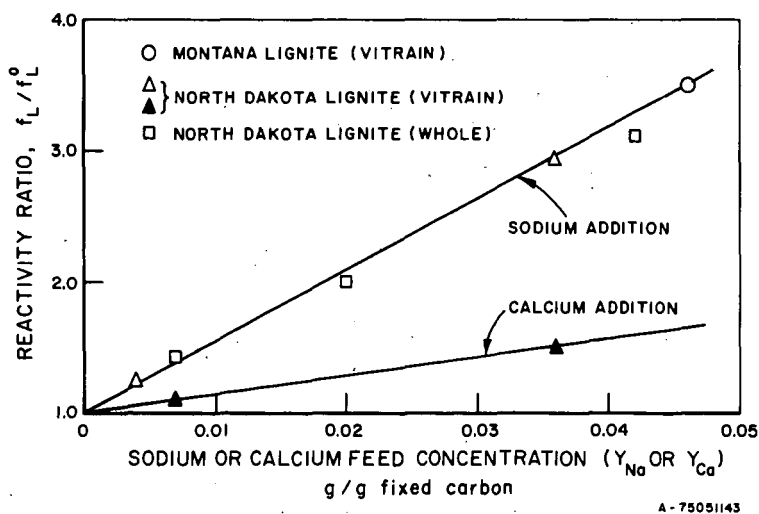

Figure 2.   CORRELATION OF
REACTIVITY FACTORS

Figure 3.   EFFECT OF CATION CONCENTRATION ON REACTIVITY
OF LIGNITE CHAR IN HYDROGEN AT 1700°F AND 35 ATMOSPHERES
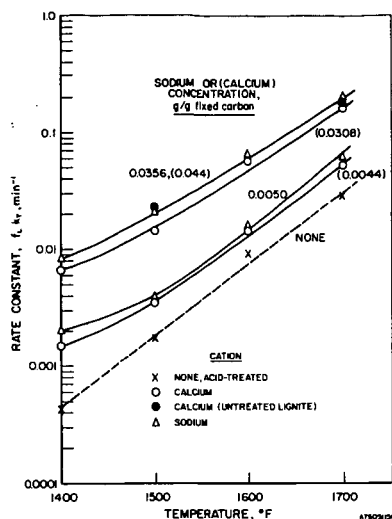
Figure 4. EFFECT OF CATION
CONCENTRATION ON REACTIVITY
OF MONTANA LIGNITE CHAR IN
STEAM-HYDROGEN MIXTURES
AT 1400° TO 1700°F AND
35 ATMOSPHERES
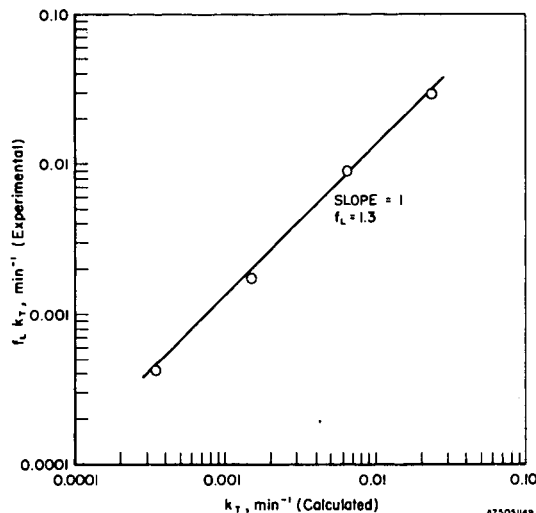
Figure 5. REACTIVITY OF ACID-TREATED
MONTANA LIGNITE CHAR IN STEAM-
HYDROGEN MIXTURES AT 1400° TO 1700°F
AND 35 ATMOSPHERES
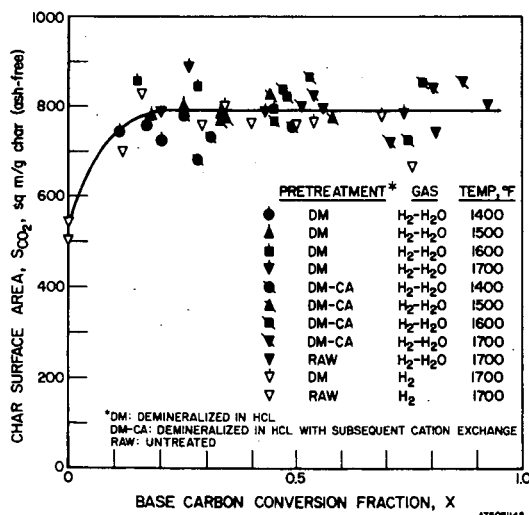
Figure 6. VARIATIONS IN SURFACE AREA MEASURED IN CARBON DIOXIDE
(S_{CO_2}) WITH BASE CARBON CONVERSION FRACTION FOR MONTANA
LIGNITE CHARS GASIFIED AT VARIOUS CONDITIONS
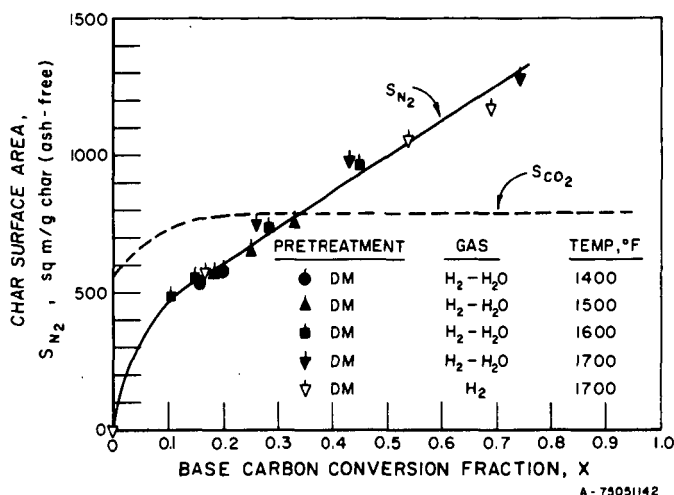
Figure 7. VARIATIONS IN APPARENT SURFACE AREA MEASURED IN
NITROGEN WITH BASE CARBON CONVERSION FRACTION FOR
MONTANA LIGNITE CHARS GASIFIED AT VARIOUS CONDITIONS
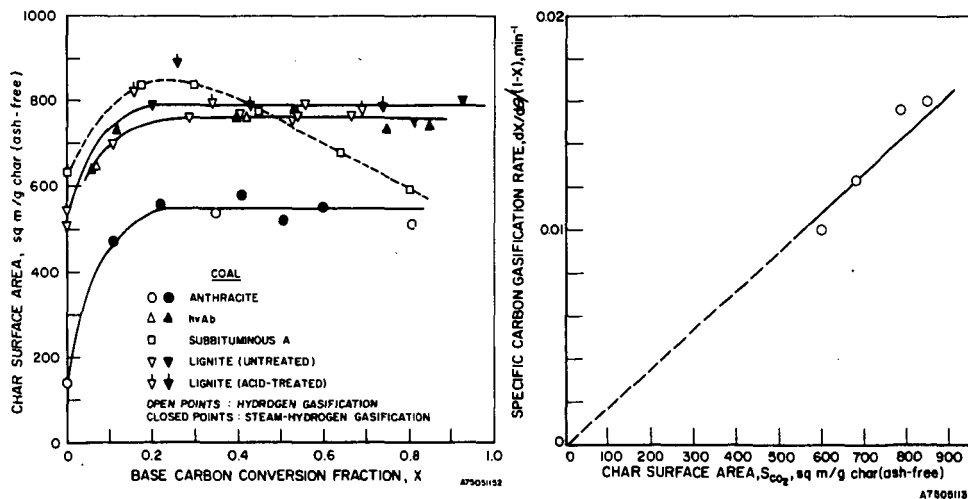
Figure 8. VARIATIONS IN S_{CO_2} WITH BASE
CARBON CONVERSION FRACTION FOR
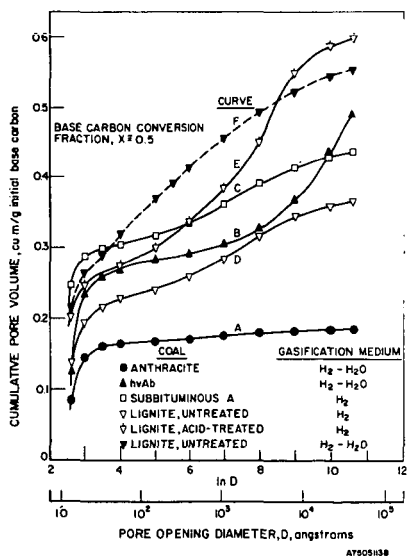DIFFERENT COAL CHARS GASIFIED IN
HYDROGEN AND STEAM-HYDROGEN
MIXTURES AT 1700°F AND 35 ATMOSPHERES

Figure 9. RELATIONSHIP BETWEEN SPECIFIC
CARBON GASIFICATION RATE AND S_{CO_2} FOR
GASIFICATION OF ROSEBUD SUBBITUMINOUS
A COAL CHAR IN HYDROGEN AT 1700°F AND
35 ATMOSPHERES
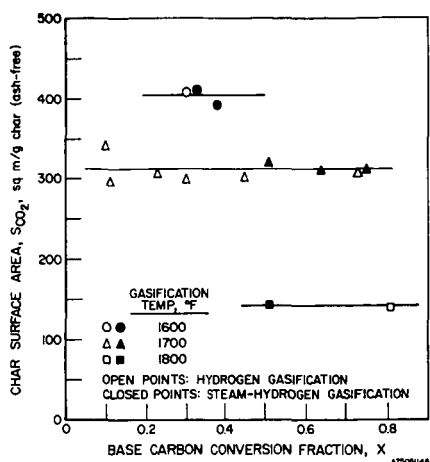
Figure 10. EFFECT OF GASIFICATION TEMPERATURE ON INTERNAL SURFACE AREA OF CARVAO METALLURGICAL COAL CHAR
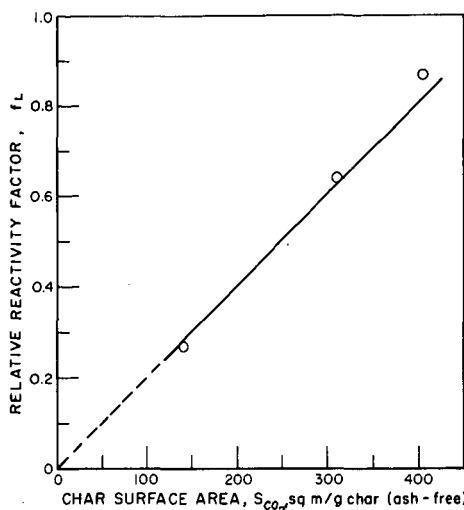
Figure 11. RELATIONSHIP BETWEEN REACTIVITY FACTOR, f_L, and S_{CO_2} FOR CARVAO METALLURGICAL COAL CHAR

Figure 12. TYPICAL PORE VOLUME DISTRIBUTIONS FOR DIFFERENT COAL CHARS GASIFIED IN HYDROGEN AND STEAM-HYDROGEN MIXTURES AT 1700°F and 35 ATMOSPHERES
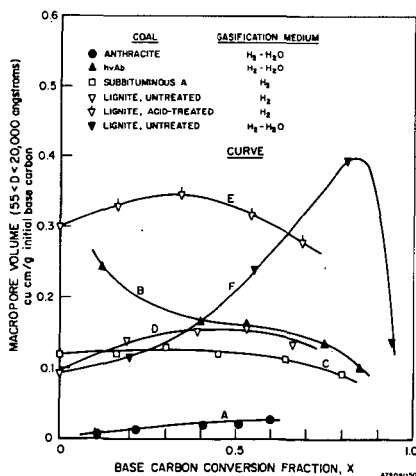

Figure 13. RELATIONSHIP BETWEEN MACROPORE VOLUME AND BASE CARBON CONVERSION FRACTION FOR DIFFERENT COAL CHARS
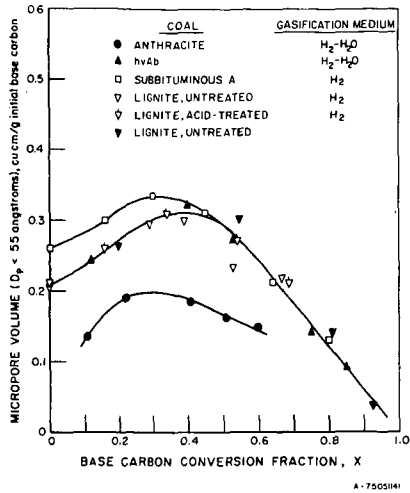
Figure 14. RELATIONSHIP BETWEEN MICROPORE VOLUME AND BASE CARBON CONVERSION FRACTION FOR DIFFERENT COAL CHARS
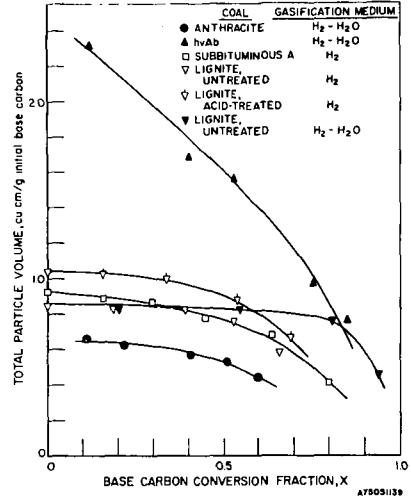
Figure 15. RELATIONSHIP BETWEEN TOTAL PARTICLE VOLUME AND BASE CARBON CONVERSION FRACTION FOR DIFFERENT COAL CHARS
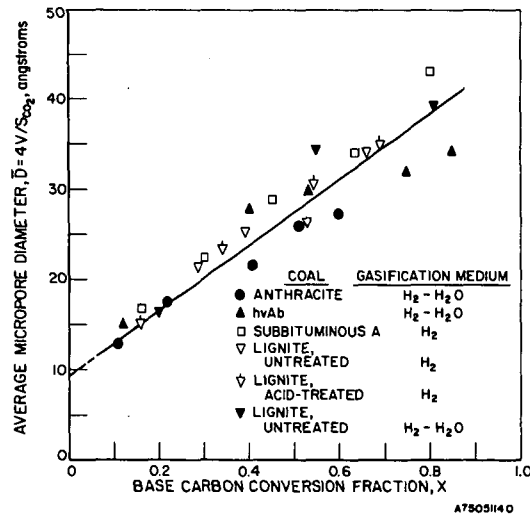

Figure 16. RELATIONSHIP BETWEEN AVERAGE MICROPORE DIAMETER AND BASE CARBON CONVERSION FRACTION FOR DIFFERENT COAL CHARS